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(54) ADHESIVE MATERIAL FILM, SEMICONDUCTOR MOUNTING EXTERNAL CONNECTING MEMBER, SEMICONDUCTOR DEVICE AND THEIR PRODUCTION

(57)Abstract:

PROBLEM TO BE SOLVED: To provide an adhesive material film difficult to generate voids in the adhesion interface and excessive squeeze-out of the adhesive material in a semiconductor device having a structure to connect

semiconductor chips with an external connecting member having a wiring which mounts the semiconductor chips by using the adhesive material film and a semiconductor mounting external connecting member excellent in reliability which uses the adhesive material film, and a semiconductor device.

SOLUTION: An adhesive material film which connects semiconductor chips with their mounting external connecting member having a wiring has adhesive layers formed on both sides of a core material having a glass transition temperature of not lower than 200°C such as polyimide, polyethersulfone, poly- amideimide, polyetheretherketone and polyetherimide with a thickness of at least one of the adhesive layers of not smaller than 30 µm and a viscosity at the contact bonding temperature of 1×105-1×107 Pa.s.

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CLAIMS

[Claim(s)]

[Claim 1] The binder film characterized by having the adhesives layer a whose viscosity in sticking-by-pressure temperature it is the binder film which connects with a semiconductor chip the member for the external connection with wiring in which this is carried, and is the range of 1x105 to 1x107Pa, and s.

[Claim 2] The binder film characterized by having the adhesives layer b whose viscosity in 100-180 degrees C it is the binder film which connects with a semiconductor chip the member for the external connection with wiring in which this is carried, and is the range of 1x105 to 1x107Pa, and s.

[Claim 3] The binder film characterized by having the adhesives layer c whose viscosity in 100-180 degrees C it is the binder film which connects with a semiconductor chip the member for the external connection with wiring in which this is carried, and is the range of 1x105 to 1x107Pa, and s.

[Claim 4] When T is made into temperature ** in the binder film which connects with a semiconductor chip the external connection member with wiring which supports this, it is eta[T] =Aexp (B/(T+273)) about viscosity Pa-s of an adhesives layer.

The binder film characterized by coming out, and having the adhesives layer d which is the range whose A is 0-10Paands and, whose B is three to 8x103 degrees C when expressed.

[Claim 5] A binder film claim 1 whose thickness of a binder film is 100-200 micrometers - given [4 each] in a term.

[Claim 6] The binder film claim 1 - given [5 each] in a term with which the binder film consists of adhesives layers a, b, and c or d.

[Claim 7] A binder film claim 1 whose binder film is a binder film which forms an adhesives layer in both sides of core material, and is obtained, whose glass transition temperature core material is heat-resistant thermoplastic FU 200 degrees C or more or a heat-resistant thermoplastic porosity film and whose thickness at least one of the adhesives layers of both sides of core material is the adhesives layers a, b, and c 30 micrometers or more or d - given [5 each] in a term.

[Claim 8] The binder film according to claim 7 whose core material is the heat-resistant thermoplastic film with which glass transition temperature is chosen from polyimide, polyether sulphone, polyamidoimide, a polyether ether ketone, or polyether imide 200 degrees C or more.

[Claim 9] The binder film according to claim 7 whose core material is the heatresistant thermoplastic porosity film chosen from polyether sulphone, polyimide polyamidoimide, polyester, or the poly ape phone.

[Claim 10] A binder film claim 7 the member for the external connection with wiring and whose adhesives layer of the side to paste up are the adhesives layers a, b, and c or d - given [9 each] in a term.

[Claim 11] A binder film claim 7 which an external connection member with wiring and the adhesives layer of the side to paste up are heat-curing system adhesives in a binder film according to claim 7, and are a semiconductor chip and the thermoplastic system adhesives with which the adhesives layer of the side to paste up contains thermoplastic system adhesives or heat-curing system resin - given [10 each] in a term.

[Claim 12] The member for external connection for semi-conductor loading which has stuck claim 1 - 11 each account binder film of a term to the semiconductor chip loading side of the member for the external connection with wiring by

pressure.

[Claim 13] The manufacturing method of the member for external connection for semi-conductor loading characterized by a sticking-by-pressure pressure carrying out thermocompression bonding in 5 or less seconds by 0.5-3.0MPa in case a binder film claim 1 - given [11 each] in a term is stuck to the semiconductor chip loading side of the member for the external connection with wiring by pressure.

[Claim 14] A semiconductor chip and the semiconductor device on which the member for the external connection with wiring was pasted up through the binder film claim 1 - given [11 each] in a term.

[Claim 15] The manufacturing method of the semiconductor device characterized by a sticking-by-pressure pressure carrying out thermocompression bonding in 5 or less seconds by 0.5-3.0MPa in case a binder film claim 1 - given [11 each] in a term is stuck to the semiconductor chip loading side of the member for the external connection with wiring by pressure.

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DETAILED DESCRIPTION

[Detailed Description of the Invention] [0001]

[Field of the Invention] This invention relates to a binder film, the member for external connection for semi-conductor loading, semiconductor devices, and those manufacturing methods.

[0002]

[Description of the Prior Art] In recent years, in connection with the densification of mounting, small and lightweight-ization are required and the semiconductor package is developed to what miniaturized the package to the almost same magnitude as a semiconductor chip. The so-called general structure of these semiconductor packages and a chip-size package (it omits Following CSP) makes the member for external connection which has a wiring layer with a binder carry out adhesion maintenance of the semiconductor chip, connects an external connection terminal with a chip electrically by various approaches, such as wire bonding and inner lead bonding of TAB (Tape Automated Bonding), and is carrying out the resin seal of a part or the whole for the package if needed further. [0003] In these semiconductor packages, the method arranged to the side to which the wiring layer of the member for external connection which consists of film substrates, such as polyimide, touches a binder is called the circuit in method. By this circuit in method, the irregularity by the pattern of the conductive layer called the land for carrying wiring and a solder ball with a thickness of about 20 micrometers in a binder film and the member front face for external connection of the side to paste up exists. Although a solder resist layer is furthermore formed on these conductive layers and concavo-convex extent may be decreasing, irregularity exists in the member front face for external connection which touches a binder film. For this reason, when carrying out thermocompression bonding of the adhesive film to the member for external connection, it is easy to produce an opening and air bubbles (for it to be described as a void below) on the outskirts of concave heights of the abovementioned member for external connection.

[0004] When there is a superfluous flash in the cutting periphery of the above-mentioned void or a binder film, this part serves as an origin and there is a problem in which big breakaway occurs in the member for external connection, a semiconductor chip, and a binder film interface, and the dependability of a package is inferior in the mounting process and temperature cycle of a package. Therefore, in case a binder film is pasted up on a wiring layer, the binder film which does not cause the superfluous flash of the above-mentioned void or a binder is needed.

[0005]

[Problem(s) to be Solved by the Invention] In case this invention carries out thermocompression bonding of the semiconductor chip to an external ****** member with wiring with a binder film, it offers the binder film which there is no void of an adhesion interface and the flash of a superfluous binder cannot generate easily.

[0006]

[Means for Solving the Problem] It depends for the lack of embedding nature of a between [wiring of the void generated in the member side for external connection, i.e. a binder film,] on sticking-by-pressure conditions, such as viscosity of the binder film in thermocompression bonding temperature, and a sticking-by-pressure pressure, sticking-by-pressure time amount, greatly. Embedded nature makes viscosity of a binder film small, or it is large in the pressure of sticking-by-pressure conditions, lengthens time amount, and can carry out improvement in things. however -- making viscosity small too much **** -- a sticking-by-pressure pressure -- since a binder film will fuse superfluously if it enlarges too much or sticking-by-pressure time amount is lengthened too much, the dimensional accuracy of a flash and a binder film deteriorates [a binder] from the film configuration before sticking by pressure. If this flash reaches to the semiconductor chip pad section, the wire bonding pad section of the member for external connection, or the inner-lead-bonding section of TAB, the bonding of it may become impossible.

[0007] this invention persons investigated the rule factor of a void and a flash produced in case the external connection member with wiring which supports a semiconductor chip and this is pasted up with a binder film. the setting range where the thickness of a sticking-by-pressure shear rate, sticking-by-pressure time amount, and a binder film etc. was restricted with workability or a package specification in fact although the parameter in sticking by pressure of a binder film could consider the thickness of the viscosity of the binder film in sticking-bypressure temperature and sticking-by-pressure temperature, a sticking-bypressure pressure, the shear rate of sticking by pressure, sticking-by-pressure time amount, and a binder film etc. -- it is applied. Therefore, the main parameters in sticking by pressure are the viscosity and the sticking-by-pressure pressures of a binder film in sticking-by-pressure temperature and sticking-bypressure temperature. However, since viscosity is expressed with the function of sticking-by-pressure temperature, an independent parameter is two, the viscosity of a binder, and a sticking-by-pressure pressure. Then, this invention persons investigated quantitatively the effect which the viscosity and the sticking-bypressure pressure of a binder have on a void and the amount of flashes using the binder film with which viscosity differs.

[0008] The binder film of this invention is a binder film which connects with a semiconductor chip the member for the external connection with wiring in which this is carried, and is characterized by having the adhesives layer a whose viscosity in sticking-by-pressure temperature is the range of 1x105 - 1x107 Pa-s. Moreover, the binder film of this invention is a binder film which connects with a semiconductor chip the member for the external connection with wiring in which this is carried, and is characterized by having the adhesives layer b whose viscosity in 100-180 degrees C is the range of 1x105 - 1x107 Pa-s. Moreover, the binder film of this invention is a binder film which connects with a semiconductor chip the member for the external connection with wiring in which this is carried, and is characterized by having the adhesives layer c whose viscosity in 100-180 degrees C is the range of 1x105 - 1x107 Pa-s. Moreover, the binder film of this

invention is eta[T] =Aexp (B/(T+273)) about viscosity Pa-s of an adhesives layer, when T is made into temperature ** in the binder film which connects with a semiconductor chip the external connection member with wiring which supports this.

It comes out, and when expressed, it is characterized by having the adhesives layer d which is the range whose A is 0 - 10 Pa-s and, whose B is three to 8x103 degrees C. As for the thickness of a binder film, it is desirable that it is 100-200 micrometers. A binder film can consist of adhesives layers a, b, and c or d. Moreover, a binder film can be a binder film which forms an adhesives layer in both sides of core material, and is obtained, core material can be [glass transition temperature 1 heat-resistant thermoplastic FU 200 degrees C or more or a heat-resistant thermoplastic porosity film, and at least one of the adhesives layers of both sides of core material can be [thickness] the adhesives layers a, b, and c 30 micrometers or more or d. The heat-resistant thermoplastic film of core material with which glass transition temperature is chosen from polyimide, polyether sulphone, polyamidoimide, a polyether ether ketone, or polyether imide 200 degrees C or more is desirable. Moreover, as for core material, it is desirable that it is the heat-resistant thermoplastic porosity film chosen from polyether sulphone, polyimide polyamidoimide, polyester, or the poly ape phone. It is desirable that the member for the external connection with wiring and the adhesives layer of the side to paste up are the adhesives layers a, b, and c or d. It is desirable that an external connection member with wiring and the adhesives layer of the side to paste up are heat-curing system adhesives, and they are a semiconductor chip and the thermoplastic system adhesives with which the adhesives layer of the side to paste up contains thermoplastic system adhesives or heat-curing system resin. As for the member for external connection of this invention for semi-conductor loading, said binder film is stuck to the semiconductor chip loading side of the member for the external connection with wiring by pressure. the time of sticking said binder film to the semiconductor chip loading side of the member for the external connection with wiring by pressure --

a sticking-by-pressure pressure -- 0.5-3.0MPa -- 5 or less seconds -- thermocompression bonding -- carrying out -- semi-conductor loading -- business -- the member for external connection -- manufacturing . The semiconductor device of this invention pastes up a semiconductor chip and the member for the external connection with wiring through said binder film. In case a semiconductor device sticks the aforementioned binder film to the semiconductor chip loading side of the member for the external connection with wiring by pressure, by 0.5-3.0MPa, in 5 or less seconds, a sticking-by-pressure pressure carries out thermocompression bonding of it, and manufactures it.

[Embodiment of the Invention] The viscosity of the adhesives layer of a binder film here is Journalof in the 1946 fiscal year. Applied Physics It defined by the 17th volume, measurement by parallel monotonous plastometer which was indicated by 458-471 pages, and the calculation value. That is, the viscosity eta of a binder film adhesive layer adds the load to the binder film of the shape of a cylinder of a radius r, and is computed from a degree type by measuring a variation rate in the height.

Eta=t/(3V2(1/Z4-Z04) /8piF) .. (1)

Here, the thickness of the binder film before Z0 adds a load, the thickness of the binder film after Z adds a load, and V are the volume of a binder film, the load F Added, and the time amount to which t added the load.

[0010] When the temperature dependence of the viscosity of a certain kind of heat-curing system binder was measured, in the limited sticking-by-pressure shear rate range, the binder film could be treated as Newtonian fluid and viscosity was expressed with temperature (T [**]) and Parameters A and B like a degree type.

eta[T] =Aexp (B/(T+273)) ... (2) [0011] Sticking-by-pressure temperature was further stuck by pressure using the binder film equipped with the adhesives layer from which viscosity differs to the member for external connection which has concave heights in the state of viscosity which changes and is different, and the

effect which it has on the void which the viscosity and the sticking-by-pressure pressure of a binder adhesives layer produce by sticking by pressure was investigated. Although detailed evaluation conditions and a detailed result were shown in the example 2 - the example 2 of a comparison, in order to have stuck the sticking-by-pressure pressure range by pressure without the void by 0.5-2.1MPa, the need for 1x107 or less Pa-s had the viscosity of a binder film adhesive layer. When dispersion in an effective pressure is not greatly desirable practically to a setting pressure in a pressure being less than 0.5 MPas, and a sticking-by-pressure pressure is too large and exceeded 2.1MPa(s), the pressure range was set to 0.5-2.1MPa here, because the land for solder ball loading may deform.

[0012] The effect which the viscosity and the sticking-by-pressure pressure of a binder adhesives layer have was similarly investigated about the amount of flashes of the binder film by sticking by pressure. Although detailed evaluation conditions and a detailed result were shown in the example 2 - the example 2 of a comparison, in order for a sticking-by-pressure pressure range to set the amount of flashes of a binder film to 50 micrometers or less by 1-2.1MPa, there was [viscosity of a binder film] the need for 1x105 or more Pa-s. As for having set the amount of flashes to 50 micrometers or less here, a binder film edge usually has the case where lead bonding becomes impossible, when 100micrometer or more binder film reaches opening for flash bondings, since it is stuck to the location which separated 50-100 micrometers from opening for bondings of an outer lead by pressure. A flash is produced in the time of pasting up a binder film on an external connection member, and the time of pasting up a semiconductor chip on a binder film further. Therefore, as for the flash in the time of sticking a binder film to an external connection member by pressure, it is desirable to be referred to as 50 micrometers or less.

[0013] In order for there to be no void of an adhesion interface from the above and to prevent the flash of a superfluous binder, it found out that it was compatible by setting preferably the viscosity in the sticking-by-pressure

temperature of a binder film adhesive layer as the range of the example of 1x105 - 1x106 Pa-s 1x105 to 1x107 Pa-s.

[0014] If the adhesives layer of a binder film can take the above-mentioned viscosity range, ******* of a binder film is [but] also good in the adhesives with which the independent film of the adhesives of the above-mentioned viscosity range can also take the above-mentioned viscosity range to both sides of core material. With the binder film in which the adhesives layer was formed especially to both sides of core material, since there is no level difference in a semiconductor chip front face in case a semiconductor chip is stuck by pressure, the adhesives layer by the side of a semiconductor chip may form adhesives other than the above-mentioned viscosity range.

[0015] The thickness of a binder film has desirable about 100-250 micrometers in the condition of having formed in core material both sides by 30 micrometers or more, when using 100-200 micrometers and core material in a binder film independent case. moreover, even if the thickness of the binder film of both sides of core material is the same, it may differ, but in order to improve the embedded nature of the binder to the wiring layer of an external connection member, binder thickness by the side of an external connection member may be made thicker than a semiconductor chip side binder.

[0016] In order to reduce the thermal stress produced from the coefficient-of-thermal-expansion difference of a semiconductor chip and a mounting substrate as a binder film, it is desirable that it is a low elastic modulus, the storage modulus at the time of measuring using a dynamic viscoelasticity measuring device is 10-2000MPa at 25 degrees C, and it is desirable that it is 3-50MPa at 260 degrees C. There is epoxy heat-curing system resin of the semi-hardening condition which consists of an epoxy resin, an epoxy group content acrylic copolymer, an epoxy resin curing agent, and an epoxy resin curing agent as a concrete example of a presentation. However, it is not limited to heat-curing system resin, and adhesives are polyimide and polyether imide. You may be thermoplastics, such as polyether amide imide.

[0017] The viscosity of a binder film adhesive layer can adjust the amount of residual solvents by the temperature at the time of the coating of an adhesives varnish, and time amount in addition to adjustment of resin combination of an adhesives presentation, or, in the case of heat-curing system resin, the semi-hardening condition can be controlled and adjusted. Moreover, it is also possible to put in and adjust organic fillers, such as inorganic fillers, such as the additive to an adhesives presentation, for example, a crystalline silica, an amorphous silica, an aluminum hydroxide, an alumina, alumimium nitride, boron nitride, and an antimony trioxide, and silicone powder.

[0018] Heat-resistant thermoplastic porosity films of glass transition temperature, such as heat-resistant thermoplastic films, such as polyimide 200 degrees C or more, a polyether ape phon, a polyamide, polyether imide, a polyester poly ape phon, a polyether ether ketone, and polyurethane, polyimide, a polyether ape phon, a polyamide, polyether imide, a polyester poly ape phon, a polyether ether ketone, and polyurethane, are [core material] desirable.

[0019] First, the connection method of the member for the external connection with wiring which supports the semiconductor chip and this by the binder film performs alignment to the member for external connection, and carries out thermocompression bonding of the binder film cut by the predetermined dimension to it. Although which approach may be used as long as cutting process is cut by the predetermined dimension, it is desirable to consider workability and to pierce using punching metal mold. Furthermore, thermocompression bonding is carried out to the binder film which has pasted up the semiconductor chip on the external connection member.

[0020] Especially although the sticking-by-pressure conditions to the member for the external connection with wiring and semiconductor chip of a binder film will not be limited especially if a binder film does not have defects, such as a void and breakaway, in an external connection member and can paste it, 100-200 degrees C of temperature are desirable [conditions] 60-250 degrees C from the heat-resistant point of the member for external connection. Its dispersion in an

actual pressure is large to a setting pressure in their being less than 0.5 MPas, and since the land for solder ball loading may deform a sticking-by-pressure pressure if 3MPa(s) are exceeded, its range of 0.5-3MPa is desirable. Moreover, sticking-by-pressure time amount considers productivity, and is desirable. [of 0.5 - 5 seconds]

[0021]

[Example] The example 1 bisphenol A mold epoxy resin (Epicoat 828, trade name by oil-ized shell epoxy incorporated company) 45 weight section, The cresol novolak mold epoxy resin (ESCN195, many names of articles by Sumitomo Chemical Co., Ltd.) 15 weight section, The phenol novolak resin (ply OFEN LF 2882, trade name by Dainippon Ink & Chemicals, Inc.) 40 weight section, The epoxy group content acrylic rubber (HTR-860P-3, trade name by imperial chemistry industrial incorporated company) 150 weight section, hardening-accelerator 1-cyanoethyl-2-phenylimidazole (cure ZORU -- 2 PZ-CN) This adhesives varnish that added the methyl ethyl ketone to the trade name by Shikoku Chemicals Corp. 0.5 weight section, and the gammaglycidoxypropyltrimetoxysilane (NUC A-187, Japanese YUMI Karr, Inc. trade name) 0.7 weight section, and carried out the churning dissolution and that was used as the adhesion varnish It applied on the polyethylene terephthalate film, stoving was carried out, and the binder film with a thickness of 50-75 micrometers was produced. At this time, it considered as the film of eight kinds (A-H) of heat-curing system resin simple substances with which the conditions of spreading heating are changed and semi-hardening conditions differ. the temperature dependence of the viscosity of these binder film -- Journal in the 1946 fiscal year of Applied the approach by the 17th volume of Physics, and the parallel monotonous plastometer indicated by 458-471 pages -- it measured. a concrete measuring method -- a binder film -- laminating -- the thickness of 500 micrometers -- carrying out -- this binder film -- the diameter of 11.3mm -- it pierced circularly, and pressurized for 10 seconds by load 8.5kgf in laying temperature, and viscosity was computed using the formula (1) from the

thickness of the binder film before and behind sticking by pressure. The temperature dependence of the viscosity of each binder film was shown in Table 1 of drawing 1.

[0022] It laminated to both sides of a 25-micrometer YUPI REXX film by having made the binder films B and C of example 2 example 1, and 75 micrometers into core material, and the binder film was produced. Thermocompression bonding was carried out to the wiring layer side of the TAB tape which consists of a polyimide system film by using 5x6mm of this binder film as an external connection member with wiring. In the width of face between wiring of 30 micrometers and the maximum **, wiring layer thickness used [the wiring width of face of a TAB tape wiring layer] the specification of 20 micrometers by 40 micrometers. Sticking-by-pressure time amount was set as for 2 seconds, and the amount of flashes after observation and sticking by pressure was measured for the void of the binder and the external connection member interface with wiring at the time of sticking a binder film by pressure to an external connection member. At the sticking-by-pressure temperature of 120-140 degrees C, a void did not occur in pressure range 1.05-1.58MPa, and the amount of flashes was also 50 micrometers or less.

[0023] The binder film with a thickness of 180 micrometers was produced for the binder films F and G of example 3 example 1, and 60 micrometers only from the binder layer in piles three layers. Thermocompression bonding was carried out to the wiring layer side of the TAB tape which consists this binder film of a polyimide system film as an external connection member with wiring like an example 2. It is **** about the amount of flashes after observation and sticking by pressure in the binder at the time of setting sticking-by-pressure time amount as for 2 seconds, and the void of an external connection member interface with wiring. At the sticking-by-pressure temperature of 120-140 degrees C, a void did not occur in pressure range 1.05-1.58MPa, and the amount of flashes was also 50 micrometers or less.

[0024] It laminated to both sides of a 25-micrometer YUPI REXX film by having

made the binder films A and D of example of comparison 1 example 1, and 75 micrometers into core material, and the binder film was produced.

Thermocompression bonding was carried out to the wiring layer side of the TAB tape which consists this binder film of a polyimide system film as an external connection member with wiring like an example 2. It is ***** about the amount of flashes after observation and sticking by pressure in the binder at the time of setting sticking-by-pressure time amount as for 2 seconds, and the void of an external connection member interface with wiring. At the sticking-by-pressure temperature of 120-140 degrees C, by pressure range 1.05-1.58MPa, the void occurred and the amount of flashes also exceeded 50 micrometers.

[0025] The binder film with a thickness of 180 micrometers was produced for the binder films E and H of example of comparison 2 example 1, and 60 micrometers only from the binder layer in piles three layers. Thermocompression bonding was carried out to the wiring layer side of the TAB tape which consists this binder film of a polyimide system film as an external connection member with wiring like an example 2. The amount of flashes after observation and sticking by pressure was measured for the binder at the time of setting sticking-by-pressure time amount as for 2 seconds, and the void of an external connection member interface with wiring. At the sticking-by-pressure temperature of 120-140 degrees C, by pressure range 1.05-1.58MPa, the void occurred and the amount of flashes also exceeded 50 micrometers.

[0026]

[Effect of the Invention] With the binder film of this invention, by setting the viscosity in thermocompression bonding temperature as the optimization range, it can connect that there are not a void of an interface and a flash of a superfluous binder in the case of adhesion with the member for the external connection with wiring, and a semiconductor chip, and the semiconductor device using the binder film and it which are excellent in dependability compared with the semiconductor device using the conventional binder film can be offered.

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DESCRIPTION OF DRAWINGS
[Brief Description of the Drawings] [Drawing 1] The table 1 showing the temperature dependence of the viscosity of each binder film.
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[Drawing 1]

表1.接着材フィルムの粘度

		粘 度:	η (T)= Λ exp (B/T)			
	100℃	120℃	140℃	160℃	A	В
Α	4.5x10 ⁶	2.8x10 ⁵	1.6x10 ⁶	1.2x10°	3.9x10 ²	3.5x10 ³
В	1.7x10 ⁶	6.6x10 ⁵	3.0x10 ⁵	1.7x10 ⁵	0.09	6.2x10 ³
С	9.9x10 ⁵	3.7x10 ⁵	1.8x10 ^s	9.8x10 ⁴	0.007	7.0x10 ³
D	2.7x10 ³	1.5x10 ³	7.4x10 ⁴	4.1x10 ⁴	0.09	5.6x10 ³
E	6.4x10 ⁶	3.0x10 ⁶	2.2x10 ⁶	2.1x10 ⁶	6.7x10 ²	3.4x10 ³
F	2.2x10 ⁶	1.1x10 ⁶	4.9x10 ⁵	2.9x10 ⁵	0.59	5.6x10 ³
G	1.1x10 ⁶	4.4x10 ⁵	2.2x10 ⁵	1.2x10 ^e	0.04	6.4x10 ³
H	2.9x10 ⁵	9.7x10 ⁴	4.6x10 ⁴	2.8x10*	0.001	7.4x10 ⁵

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(54) 【発明の名称】 接着材フィルム、半導体搭載用外部接続用部材、半導体装置及びそれらの製造法

(57)【要約】

【課題】 半導体チップとこれを搭載する配線付外部接続部材を接着材フィルムで接続する構造の半導体装置において、接着界面のボイドや接着材の過剰なはみ出しが発生しにくい接着材フィルムおよびそれを用いた信頼性に優れる半導体搭載用外部接続用部材、半導体装置を提供する。

【解決手段】 半導体チップとこれを搭載する配線付外部接続用部材を接続する接着材フィルムであって、ガラス転移温度が200 C以上のポリイミド、ポリエーテルスルホン、ポリアミドイミド、ポリエーテルエーテルケトン又はポリエーテルイミド等のコア材の両面に接着剤層が形成されており、接着剤層の少なくとも一つが厚み 30μ M以上で、圧着温度での粘度が $1\times10^5\sim1\times10^7$ Pa·s接着剤層を備える。

【特許請求の範囲】

【請求項1】 半導体チップとこれを搭載する配線付外部接続用部材を接続する接着材フィルムであって、圧着温度での粘度が $1 \times 10^5 \sim 1 \times 10^7 \, \mathrm{Pa} \cdot \mathrm{s}$ の範囲である接着剤層aを備えることを特徴とする接着材フィルム、

【請求項2】 半導体チップとこれを搭載する配線付外部接続用部材を接続する接着材フィルムであって、 $100\sim180$ での粘度が $1\times10^5\sim1\times10^7$ Pa·sの範囲である接着剤層bを備えることを特徴とする接着材フィルム。

【請求項3】 半導体チップとこれを搭載する配線付外部接続用部材を接続する接着材フィルムであって、 $100\sim180$ での粘度が $1\times10^5\sim1\times10^7$ Pa·sの範囲である接着剤層 cを備えることを特徴とする接着材フィルム。

【請求項4】 半導体チップとこれを支持する配線付外 部接続部材を接続する接着材フィルムにおいて、Tを温 度でとすると接着剤層の粘度Pa・sを

 $\eta [T] = A e x p (B/(T+273))$

で表したとき、Aが0~10Pa・sでかつBが3~8 ×10³℃の範囲である接着剤層dを備えることを特徴 とする接着材フィルム。

【請求項5】 接着材フィルムの厚さが100~200 μmである請求項1~4各項記載の接着材フィルム。

【請求項6】 接着材フィルムが接着剤層a、b、c又はdで構成されている請求項1~5各項記載の接着材フィルム。

【請求項7】 接着材フィルムが、コア材の両面に接着 剤層を形成して得られる接着材フィルムであり、コア材 がガラス転移温度が200℃以上の耐熱性熱可塑フ又は 耐熱性熱可塑多孔質フィルムであり、コア材の両面の接着剤層の少なくとも一つが厚みが30μm以上の接着剤層a、b、c又はdである請求項1~5各項記載の接着 材フィルム。

【請求項8】 コア材が、ガラス転移温度が200℃以上のポリイミド、ポリエーテルスルホン、ポリアミドイミド、ポリエーテルエーテルケトン又はポリエーテルイミドから選ばれる耐熱性熱可塑フィルムである請求項7記載の接着材フィルム。

【請求項9】 コア材が、ポリエーテルサルホン、ポリイミドポリアミドイミド、ポリエステル又はポリサルホンから選ばれる耐熱性熱可塑多孔質フィルムである請求項7記載の接着材フィルム。

【請求項10】 配線付外部接続用部材と接着する側の接着剤層が、接着剤層a、b、c又はdである請求項7~9各項記載の接着材フィルム。

【請求項11】 請求項7記載の接着材フィルムにおいて配線付外部接続部材と接着する側の接着剤層が熱硬化系接着剤であり、半導体チップと接着する側の接着剤層

が熱可塑系接着剤または熱硬化系樹脂を含む熱可塑系接着剤である請求項7~10各項記載の接着材フィルム。

【請求項12】 配線付外部接続用部材の半導体チップ 搭載面に請求項1~11各項記接着材フィルムが圧着し てある半導体搭載用外部接続用部材。

【請求項13】 配線付外部接続用部材の半導体チップ 搭載面に請求項1~11各項記載の接着材フィルムを圧 着する際、圧着圧力が0.5~3.0MPaで5秒以下 で熱圧着することを特徴とする半導体搭載用外部接続用 部材の製造法。

【請求項14】 半導体チップと配線付外部接続用部材を請求項1~11各項記載の接着材フィルムを介して接着した半導体装置。

【請求項15】 配線付外部接続用部材の半導体チップ 搭載面に請求項1~11各項記載の接着材フィルムを圧 着する際、圧着圧力が0.5~3.0MPaで5秒以下 で熱圧着することを特徴とする半導体装置の製造法。

【発明の詳細な説明】

[0001]

【発明の属する技術分野】本発明は、接着材フィルム、 半導体搭載用外部接続用部材、半導体装置及びそれらの 製造法に関する。

[0002]

【従来の技術】近年、半導体パッケージは実装の高密度化に伴い、小型、軽量化が要求され、パッケージを半導体チップとほぼ同じ大きさまで小型化したものまで開発されている。これら半導体パッケージ、いわゆるチップサイズパッケージ(以下CSPと略す)の一般的な構造は、半導体チップを接着材により配線層を有する外部接続用部材に接着保持させ、チップと外部接続端子をワイヤーボンディングやTAB(Tape Automated Bonding)のインナーリードボンディング等各種方法により電気的に接続し、さらに必要に応じてパッケージを一部又は全体を樹脂封止している。

【0003】これら半導体パッケージにおいて、ポリイミド等のフィルム基板からなる外部接続用部材の配線層が接着材と接する側に配置している方式はサーキットイン方式と呼ばれている。このサーキットイン方式では接着材フィルムと接着する側の外部接続用部材表面に、厚み20μm程度の配線やはんだボールを搭載するためのランドと呼ばれる導電層のパターンによる凹凸が存在する。さらにこれら導電層の上にソルダレジスト層が形成され、凹凸の程度が低減している場合もあるが、接着材フィルムと接する外部接続用部材表面には凹凸が存在する。このため外部接続用部材へ接着フィルムを熱圧着する場合、上記外部接続用部材の凹凸部周辺に空隙や気泡(以下ボイドと記す)が生じ易い。

【0004】上記ボイドや接着材フィルムの切断周辺部での過剰なはみ出しがあると、この部分が起点となりパッケージの実装過程や温度サイクルにおいて、外部接続

用部材や半導体チップと接着材フィルム界面で大きなは く離が発生しパッケージの信頼性が劣る問題がある。し たがって接着材フィルムを配線層へ接着する際に、上記 ボイドや接着材の過剰なはみ出しを起こさない接着材フィルムが必要となる。

[0005]

【発明が解決しようとする課題】本発明は、配線付外部接用続部材と半導体チップを接着材フィルムで熱圧着する際に、接着界面のボイドがなくかつ過剰な接着材のはみ出しが発生しにくい接着材フィルムを提供するものである。

[0006]

【課題を解決するための手段】外部接続用部材側に発生するボイド、すなわち接着材フィルムの配線間への埋め込み性不足は、熱圧着温度での接着材フィルムの粘度や、圧着圧力および圧着時間等の圧着条件に大きく依存する。埋込性は、接着材フィルムの粘度を小さくしたり、圧着条件の圧力を大きく、時間を長くすること向上できる。しかし粘度を小さくし過ぎたり、圧着圧力大きくし過ぎたり、圧着時間を長くし過ぎると接着材フィルムが過剰に溶融するため、圧着前のフィルム形状より接着材がはみ出し、接着材フィルムの寸法精度が劣化する。このはみ出しが半導体チップパッド部や外部接続用部材のワイヤーボンディングパッド部やTABのインナーリードボンディング部まで達すると、ボンディングが不可能となる場合がある。

【0007】本発明者らは、半導体チップとこれを支持 する配線付外部接続部材を接着材フィルムで接着する際 に生ずる、ボイドとはみ出しの支配因子を調べた。接着 材フィルムの圧着におけるパラメータは、圧着温度、圧 着温度での接着材フィルムの粘度、圧着圧力、圧着の剪 断速度、圧着時間、接着材フィルムの厚み等が考えられ るが、実際には圧着剪断速度、圧着時間、接着材フィル ムの厚み等は作業性やパッケージ仕様により限られた設 定範囲、運用されている。したがって、圧着における主 なパラメータは圧着温度、圧着温度での接着材フィルム の粘度および圧着圧力である。しかし粘度は圧着温度の 関数で表されるので、独立なパラメータは接着材の粘度 と圧着圧力の二つである。そこで本発明者らは粘度の異 なる接着材フィルムを用い、接着材の粘度と圧着圧力が ボイドとはみ出し量にあたえる影響を定量的に調べた。 【0008】本発明の接着材フィルムは、半導体チップ とこれを搭載する配線付外部接続用部材を接続する接着 材フィルムであって、圧着温度での粘度が1×105~ 1 x 1 O⁷ P a · s の範囲である接着剤層 a を備えるこ とを特徴とする。また、本発明の接着材フィルムは、半 導体チップとこれを搭載する配線付外部接続用部材を接

続する接着材フィルムであって、100~180℃での

粘度が1x10⁵~1x10⁷Pa·sの範囲である接着

剤層bを備えることを特徴とする。また、本発明の接着

材フィルムは、半導体チップとこれを搭載する配線付外部接続用部材を接続する接着材フィルムであって、100~180℃での粘度が1×105~1×107Pa・sの範囲である接着剤層cを備えることを特徴とする。また、本発明の接着材フィルムは、半導体チップとこれを支持する配線付外部接続部材を接続する接着材フィルムにおいて、Tを温度℃とすると接着剤層の粘度Pa・sを

 $\eta [T] = A e x p (B/(T+273))$ で表したとき、Aが $0\sim10$ $Pa\cdot s$ でかつBが $3\sim8$ ×10³℃の範囲である接着剤層dを備えることを特徴 とする。接着材フィルムの厚さは、100~200μm であることが好ましい。接着材フィルムは、接着剤層 a、b、c又はdで構成されることができる。また、接 着材フィルムは、コア材の両面に接着剤層を形成して得 られる接着材フィルムであり、コア材がガラス転移温度 が200℃以上の耐熱性熱可塑フ又は耐熱性熱可塑多孔 質フィルムであり、コア材の両面の接着剤層の少なくと も一つが厚みが30μm以上の接着剤層a、b、c又は dであることができる。コア材は、ガラス転移温度が2 00℃以上のポリイミド、ポリエーテルスルホン、ポリ アミドイミド、ポリエーテルエーテルケトン又はポリエ ーテルイミドから選ばれる耐熱性熱可塑フィルムが好ま しい。またコア材は、ポリエーテルサルホン、ポリイミ ドポリアミドイミド、ポリエステル又はポリサルホンか ら選ばれる耐熱性熱可塑多孔質フィルムであることが好 ましい。配線付外部接続用部材と接着する側の接着剤層 が、接着剤層a、b、c又はdであることが好ましい。 配線付外部接続部材と接着する側の接着剤層が熱硬化系 接着剤であり、半導体チップと接着する側の接着剤層が 熱可塑系接着剤または熱硬化系樹脂を含む熱可塑系接着 剤であることが好ましい。本発明の半導体搭載用外部接 続用部材は、配線付外部接続用部材の半導体チップ搭載 面に前記接着材フィルムが圧着してある。配線付外部接 続用部材の半導体チップ搭載面に前記接着材フィルムを 圧着する際、圧着圧力が0.5~3.0MPaで5秒以 下で熱圧着し半導体搭載用外部接続用部材の製造する。 本発明の半導体装置は、半導体チップと配線付外部接続 用部材を前記接着材フィルムを介して接着したものであ る。半導体装置は、配線付外部接続用部材の半導体チッ プ搭載面に前記の接着材フィルムを圧着する際、圧着圧

[0009]

する。

【発明の実施の形態】ここでの接着材フィルムの接着剤層の粘度は1946年度のJournalof Applied Physics 第17巻、458~471ページに記載されたような平行平板プラストメータ法による測定、算出値で定義した。すなわち接着材フィルム接着剤層の粘度のは、半径rの円柱状の接着材フィルム

力がO.5~3.0MPaで5秒以下で熱圧着して製造

に荷重を加えていき、その高さ変位を測定することによ

 $\eta = t / (3V^2 (1/Z^4 - ZO^4) / 8\pi F)) \cdot \cdot (1)$

ここで、Z0は荷重を加える前の接着材フィルムの厚さ、Zは荷重を加えた後の接着材フィルムの厚さ、Vは接着材フィルムの体積、F加えた荷重、tは荷重を加えた時間である。

【0010】ある種の熱硬化系接着材の粘度の温度依存

【0011】粘度の異なる接着剤層を備えた接着材フィルムを用い、さらに圧着温度を変えて異なる粘度の状態で凹凸部のある外部接続用部材へ圧着し、接着材接着剤層の粘度と圧着圧力が圧着により生ずるボイドに与える影響を調べた。詳しい評価条件および結果は実施例2~比較例2に示すが、圧着圧力範囲が0.5~2.1MPaでボイドなく圧着するには、接着材フィルム接着剤層の粘度が1×10⁷Pa・s以下の必要があった。ここで圧力範囲を0.5~2.1MPaとしたのは、圧力が0.5MPa未満であると設定圧力に対し実効圧力のばらつきが大きく実用上好ましくなく、また圧着圧力が大きすぎ2.1MPaを超えるとはんだボール搭載用のランド部が変形する場合があるためである。

【0012】同様に圧着による接着材フィルムのはみ出 し量に関しても、接着材接着剤層の粘度と圧着圧力が与 える影響を調べた。詳しい評価条件および結果は実施例 2~比較例2に示すが、圧着圧力範囲が1~2.1MP aで接着材フィルムのはみ出し量を50μm以下にする ためには、接着材フィルムの粘度が1x10⁵Pa・s 以上の必要があった。ここではみ出し量を50μm以下 としたのは、通常接着材フィルム端はアウターリードの ボンディング用開口部から50~100μm離れた位置 に圧着されているので100μm以上接着材フィルムが はみ出しボンディング用開口部に達すると、リードボン ディングができなくなる場合がある。はみ出しは接着材 フィルムを外部接続部材に接着する際と、さらに半導体 チップを接着材フィルムに接着する際で生じる。したが、 って、接着材フィルムを外部接続部材に圧着した時点で のはみ出しは50μm以下とするのが望ましい。

【0013】上記より接着界面のボイドがなくかつ過剰な接着材のはみ出しを防ぐためには、接着材フィルム接着剤層の圧着温度での粘度を $1 \times 10^5 \sim 1 \times 10^7 \, \mathrm{Pa}$ ・s、好ましくは $1 \times 10^5 \sim 1 \times 10^6 \, \mathrm{Pa}$ ・sの範の範囲に設定することにより両立できることを見いだした。

【0014】接着材フィルムの接着剤層が上記粘度範囲をとりえれば接着材フィルムは、上記粘度範囲の接着剤の単独フィルムでも、コア材の両面に上記粘度範囲をとりえる接着剤を形成したもでもよい。特にコア材の両面に接着剤層を形成した接着材フィルムでは、半導体チップを圧着する際には半導体チップ表面に段差がないので、半導体チップ側の接着剤層は上記粘度範囲以外の接

性を測定したところ、限られた圧着剪断速度範囲では接着材フィルムはニュートン流体として扱えられ、粘度は次式のように温度(T [$^{\circ}$])およびパラメータA及びBで表された。

 $\eta [T] = A e x p (B/(T+273)) \cdot \cdot \cdot (2)$

着剤を形成してもよい。

り次式から算出される。

【0015】接着材フィルムの厚みは接着材フィルム単独の場合100~200μm、コア材を用いる場合は30μm以上でコア材両面に形成した状態で100~250μm程度が好ましい。また、コア材の両面の接着材フィルムの厚みは同じでも異なっていてもよいが、外部接続部材の配線層への接着材の埋込性を向上するために外部接続部材側の接着材厚みを半導体チップ側接着材より厚くしてもよい。

【0016】接着材フィルムとしては、半導体チップと 実装基板の熱膨張係数差から生ずる熱応力を低減するために低弾性率であることが好ましく、動的粘弾性測定装 置を用いて測定した場合の貯蔵弾性率が25℃で10~ 2000MPaであり、260℃で3~50MPaであ ることが好ましい。具体的な組成例としてはエポキシ樹 脂、エポキシ基含有アクリル共重合体、エボキシ樹脂硬 化剤およびエポキシ樹脂硬化剤からなる半硬化状態のエ ポキシ熱硬化系樹脂がある。しかし、接着剤は熱硬化系 樹脂に限定されることはなく、ボリイミド、ボリエーテ ルイミド。ボリエーテルアミドイミド等の熱可塑性樹脂 であってもよい。

【0017】接着材フィルム接着剤層の粘度は接着剤組成の樹脂配合の調整以外に、接着剤ワニスの塗工時の温度、時間により残存溶媒量を調整したり、熱硬化系樹脂の場合はその半硬化状態を制御して調整することができる。また接着剤組成への添加剤、例えば結晶性シリカ、非晶性シリカ、水酸化アルミニウム、アルミナ、窒化アルミニウム、窒化ホウ素、三酸化アンチモン等の無機フィラーやシリコーンパウダー等の有機フィラーを入れて調整することも可能である。

【0018】コア材はガラス転移温度が200℃以上のポリイミド、ポリエーテルサルフォン、ポリアミド、ポリエーテルイミド、ポリエステルポリサルフォン、ポリエーテルエーテルケトン、ポリウレタン等の耐熱性熱可塑フィルムやボリイミド、ポリエーテルサルフォン、ポリアミド、ポリエーテルイミド、ポリエステルポリサルフォン、ポリエーテルエーテルケトン、ポリウレタン等耐熱性熱可塑多孔質フィルムが好ましい。

【0019】接着材フィルムによる半導体チップとこれを支持する配線付外部接続用部材の接続方法は、まず外部接続用部材へ所定の寸法に切断された接着材フィルムを位置合わせを行い熱圧着する。切断方法は所定の寸法

に切断されればいづれの方法でも構わないが、作業性を 考え打ち抜き金型を用いて打ち抜くことが望ましい。さ らに半導体チップを、外部接続部材へ接着してある接着 材フィルムへ熱圧着する。

【0020】接着材フィルムの配線付外部接続用部材および半導体チップへの圧着条件は、接着材フィルムが外部接続部材にボイドやはく離等の欠陥がなく接着できれば特に限定されないが、温度は外部接続用部材の耐熱性の点から60~250℃、特に100~200℃が好ましい。圧着圧力は0.5MPa未満であると設定圧力に対し実際の圧力のばらつきが大きく、また3MPaを超えるとはんだボール搭載用のランド部が変形する場合があるので、0.5~3MPaの範囲が好ましい。また圧着時間は生産性を考え0.5~5秒が好ましい。

[0021]

【実施例】実施例1

ビスフェノールA型エポキシ樹脂 (エピコート828、 油化シェルエポキシ株式会社製商品名)45重量部、ク レゾールノボラック型エポキシ樹脂(ESCN195、 住友化学工業株式会社製諸品名)15重量部、フェノー ルノボラック樹脂(プライオーフェンLF2882、大 日本インキ化学工業株式会社製商品名)40重量部、エ ポキシ基含有アクリルゴム(HTR-860P-3、帝 国化学産業株式会社製商品名)150重量部、硬化促進 剤1-シアノエチル-2-フェニルイミダゾール(キュ アゾール2PZ-CN、四国化成工業株式会社製商品 名)0.5重量部、 γ -グリシドキシプロピルトリメト キシシラン(NUC A-187、日本ユミカー株式会 社製商品名) 〇. 7重量部にメチルエチルケトンを加え て撹拌溶解し接着ワニスとした、この接着剤ワニスを、 ポリエチレンテレフタレートフィルム上に塗布し加熱乾 燥して厚み50~75μmの接着材フィルムを作製し た。この時、塗布加熱の条件を変え半硬化状態の異な る、8種類(A~H)の熱硬化系樹脂単体のフィルムと した。これら接着材フィルムの粘度の温度依存性を19 46年度のJournal of Applied P hysics第17巻、458~471ページに記載さ れた平行平板プラストメータによる方法での測定した。 具体的な測定方法は、接着材フィルムをラミネートし厚 み500μmとし、この接着材フィルムを直径11.3 mmの円形に打ち抜き、設定温度において荷重8.5k gfで10秒間加圧し、圧着前後の接着材フィルムの厚 みから式(1)を用いて粘度を算出した。図1の表1に 各接着材フィルムの粘度の温度依存性を示した。

【0022】実施例2

実施例1の接着材フィルムB、C、75μmをコア材として25μmのユーピレックスフィルムの両面にラミネートして接着材フィルムを作製した。この接着材フィルム5x6mmを配線付き外部接続部材としてポリイミド系フィルムからなるTABテープの配線層面に熱圧着を

行った。TABテープ配線層の配線幅は 30μ m、最狭の配線間幅は 40μ mで配線層厚みは 20μ mの仕様を用いた。圧着時間を2秒間とし、接着材フィルムを外部接続部材へ圧着した際の、接着材と配線付き外部接続部材界面のボイドを観察及び圧着後のはみ出し量を測定した。圧着温度 $120\sim140$ °Cで、圧力範囲 $1.05\sim1.58$ MPaで、ボイドが発生せず、かつはみ出し量も 50μ m以下であった。

【0023】実施例3

実施例1の接着材フィルムF、G、60μmを3層重ねて接着材層のみから厚み180μmの接着材フィルムを作製した。この接着材フィルムを実施例2と同様に配線付き外部接続部材としてポリイミド系フィルムからなるTABテープの配線層面に熱圧着を行った。圧着時間を2秒間とした場合の接着材と配線付き外部接続部材界面のボイドを観察及び圧着後のはみ出し量を測た。圧着温度120~140℃で、圧力範囲1.05~1.58MPaで、ボイドが発生せず、かつはみ出し量も50μm以下であった。

【0024】比較例1

実施例1の接着材フィルムA、D、 75μ mをコア材として 25μ mのユーピレックスフィルムの両面にラミネートして接着材フィルムを作製した。この接着材フィルムを実施例2と同様に配線付き外部接続部材としてポリイミド系フィルムからなるTABテープの配線層面に熱圧着を行った。圧着時間を2秒間とした場合の接着材と配線付き外部接続部材界面のボイドを観察及び圧着後のはみ出し量を測定た。圧着温度 $120\sim140$ °Cで、圧力範囲 $1.05\sim1.58$ MPaで、ボイドが発生し、かつはみ出し量 50μ mを超えた。

【0025】比較例2

実施例1の接着材フィルムE、H、60 μ mを3層重ねて接着材層のみから厚み180 μ mの接着材フィルムを作製した。この接着材フィルムを実施例2と同様に配線付き外部接続部材としてポリイミド系フィルムからなるTABテープの配線層面に熱圧着を行った。圧着時間を2秒間とした場合の接着材と配線付き外部接続部材界面のボイドを観察及び圧着後のはみ出し量を測定した。圧着温度120~140 Γ で、圧力範囲1.05~1.58MPaで、ボイドが発生し、かつはみ出し量も50 μ mを超えた。

[0026]

【発明の効果】本発明の接着材フィルムでは熱圧着温度での粘度を最適化範囲に設定することにより、配線付外部接続用部材と半導体チップとの接着の際に界面のボイドおよび過剰な接着材のはみ出し無く接続することができ、従来の接着材フィルムを用いた半導体装置に比べて信頼性に優れる接着材フィルムおよびそれを用いた半導体装置を提供することができる。

【図面の簡単な説明】

【図1】 各接着材フィルムの粘度の温度依存性を示す 表1。

【図1】

表1.接着材フィルムの粘度

	1	粘 度:	η (T)= A exp (B/1)			
	100℃	120°C	140℃	160℃	A	В
Α	4.5x10⁵	2,8x10 ⁵	1.6x10 ⁶	1.2x10 ⁶	3.9x10 ²	3.5x10 ³
В	1.7x10 ⁶	6.6x10 ⁵	3.0x10 ³	1.7x10 ⁵	0.09	6.2x10 ³
С	9.9x10 ⁵	3.7x10 ⁵	1.8x10 ⁵	9.8x10 ⁴	0.007	7.0x10 ³
D	2.7x10 ³	1.5x10 ⁵	7.4x10 ⁴	4.1x10 ⁴	0.09	5.6x10 ³
E	6.4x10 ⁶	3.0x10 ⁵	2.2x10 ⁶	2,1x10 ⁶	6.7x10 ²	3.4x10 ³
F	2.2x10 ⁶	1.1x10 ⁶	4.9x10 ⁵	2.9x10 ⁵	0.59	5.6x10 ³
G	1.1x10 ⁶	4.4x10 ⁵	2.2x10 ⁵	1.2x10 ⁴	0.04	6.4x10 ³
H	2.9x10 ⁵	9.7x10 ⁴	4.6x10 ⁴	2.8x10 ⁴	0.001	7.4x10 ³

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AK53D AK54E AK55E AK56E

ALO5A ALO5B ALO5C ALO5D

ANO2A ANO2B ANO2C ANO2D

AROOA AROOB AROOC ATOOE

BA05 BA07 BA13 BA15 DJ01E

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